DISPOSABLE CATALYSTS IN TWO-STAGE COAL LIQUEFACTION

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Introduction

In Two Stage Liquefaction, coal is dissolved and partially hydrogenated in the short contact time first stage using process derived solvent as vehicle oil. The unreacted coal and ash are removed by antisolvent deashing and the product oil is upgraded in a separate catalytic reactor (Stage II). This scheme is proposed as a means of converting coal to distillate with higher yield, reduction in hydrogen consumption, and minimal catalyst poisoning since no catalyst is used in the first stage. A number of papers have been published discussing various aspects of this technique (1,2,3,4,5).

In this investigation a disposable ore catalyst consisting of a mixture of bauxite, limonite, and molybdenum ore concentrate is added to the first stage and its effect on the yield and quality of the product oil from the second stage is studied.

Rationale for the Use of Ores as Catalysts

Our research work (6,7) as well as a literature review reveals that cobalt and molybdenum are eminently suited catalysts for hydrogenation and hydrodesulfurization of coal, whereas nickel and molybdenum are good for hydrodenitrogenation. Other metals like iron, copper, tin, zinc, platinum, and tungston have also been found to be effective in coal liquefaction (8). The most inexpensive sources of these metals are their ores where they are present mostly as sufides or oxides.

A number of researchers (9,10) have shown iron pyrites to be an effective catalyst in coal liquefaction. Our earlier studies (11,12,13) have shown that mixtures of iron pyrites and minerals containing other catalytic active transition metals were better liquefaction catalysts than iron pyrites alone. The best ore catalysts tested, in terms of high liquid yield and low product oil viscosities, were mixtures of pyrites, molybdenum ore concentrate, and cobalt-containing ores.

In this study an acid treated (14) mixture of bauxite, limonite and molybdenum ore concentrate was used as a disposable catalyst in the first stage. In the second stage a commercial supported nickel-molybdenum catalyst was used for hydroprocessing.

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Materials, Experimental Equipment, and Experimental Procedure

The major materials used in this study consisted of bituminous coal, a coal-derived heavy distillate, and a disposable ore catalyst. Bitminous coal from the Blacksville No. 2 mine, West Virginia (Pittsburgh seam) whose proximate and ultimate analyses are presented in Table I was used. The vehicle oil was distillate with a boiling range 232-455°C produced at the Ft. Lewis pilot plant running in the SRC-II mode.

A mixture of acid treated bauxite, limonite, and molybdenum ore concentrate (analyses of ores given in Table II) was used as a disposable catalyst in Stage I. A commercially available supported Ni-Mo-alumina catalyst from American Cynamid Co. (HDS-3) was used as a hydroprocessing catalyst for the Stage II. The catalyst and coal used were ground to minus 200 mesh. Hydrogen gas of > 99.95% purity was used.

Experimental Equipment

The hydrogenation reaction was carried out in a stainless steel liner placed in a high pressure internally stirred autoclave of one liter capacity. The experiments were carried out at a stirrer speed of 1000 rpm. The autoclave was provided with a cooling coil through which water could be passed to reduce the reaction temperature if so desired. The autoclave had an electric furnace controlled with a proportional temperature controller. The temperature of the reaction mass was continuously monitored by a temperature recorder. In addition, the autoclave was provided with a thermowell, a pressure gauge, a vent, a sampling valve, and a safety rupture disc. A compressor was used to pressurize the autoclave with hydrogen.

Experimental Procedure

Each of the experimental runs consisted of two stages. In the first, SRC-II distillate was used as the vehicle while in the second, the liquid product from the first stage was used instead. This procedure was followed to approximate the use of product oil from the Stage I for hydroprocessing in Stage II.

Stage I Liquefaction: Forty grams of crushed coal were placed in the liner. About 83.6 gms of SRC-II distillate (in approximately 1:2.1 ratio) were then added to the liner. A pre-determined amount of the disposable ore catalyst was next added to the contents of the liner. The stirrer assembly was fitted onto the autoclave and securely bolted. After testing for leakage, the autoclave was purged with hydrogen. It was then pressurized to a predetermined value so that a pressure of about 2000 psig (13.79 MPa) was reached at the reaction temperature. The heating was initiated thereafter. It usually took 65-70 minutes to heat the autoclave and its contents from room temperature to reaction temperature. The reaction was then allowed to proceed for a given period of time. The temperature was maintained at the reaction temperature during this period. After the elapse of reaction time, the reaction was arrested by turning off the power to the furnace and cooling the contents down rapidly by passing cold water through the cooling coil. The autoclave was allowed to cool down to room temperature by leaving it overnight. The lique-

Table I

Proximate and Ultimate Analyses of Coal Sample

Proximate Analysis	As Recd. %	Moist. Free %	Moist., Ash Free %
Moisture	1.2	N/A	N/A
Volatile	35.8	36.2	41.0
Fixed Carbon	51.5	52.1	59.0
Ash	11.5	11.7	N/A

Ultimate Analysis	As Recd. %	Moist. Free %	Moist., Ash Free %
Hydrogen	5.0	4.9	5.5
Carbon	72.0	72.9	82.5
Nitrogen	1.0	1.2	1.4
Sulfur	2.7	2.7	3.1
Oxygen	7.7	6.7	7.6
Ash	11.5	11.7	N/A
Btu/lbm	12,892	13,052	14,776

Table II

Mineral Ores and Their Percent Composition

1.	Limonite	Ni	1.1	Si	16.4
		Mg	9.8	Fe	20.2
		Al	1.4	Cr	0.5
2.	Molybdenum Oxide Concentrate (Moly. Corp.)	Mo	47.0	Ca	0.4
		Fe	2.8	Cu	0.5
		Si	3.5	Sn	0.4
		Mg	0.6	Zn	0.2
		Al	0.6	K	0.2
		S	0.4		
3.	Bauxite (Canada)	Mn	0.1	Si	1.9
		Ni	0.5	Ca	0.3
		S	0.1	Co	0.1
		Sn	0.7	Al	28.8
		Ti	10.1	Cr	0.3
		Mo	0.2	Cu	0.1
		Ag	0.1	Fe	5.6
		Na	0.6	K	0.3
				Mg	0.1

fied products were then taken out of the autoclave and hot filtered to remove unconverted coal, ash, and catalyst. The filtered liquid and residue were weighed and percent conversion and liquefaction calculated. Viscosity of the product liquid at 60°C was determined using a Brookfield viscometer.

Stage II Liquefaction: The same procedure was repeated using filtered product liquid from the Stage I. A commercial supported Ni-Mo catalyst was used for this stage.

Results and Discussion

The main objective of this investigation was to study the effect of addition of a disposable catalyst in the Stage I on the yield and quality of product oil from the Stage II. The percent conversion, percent oil yield and viscosity of the product oils are presented in Table III.

Percent conversion and liquefaction of coal are defined as follows:

Percent Conversion = {Original Coal (macf) - Residue (macf)} x 100/Original Coal (macf)

Percent Liquefaction = Liquid Products x 100/Original Coal (macf)

where macf = moisture, ash, catalyst free

Experiments S.N. 1 through 12 show the effect of addition of a disposable catalyst to Stage I. Experiments were conducted at reaction time of 30, 10, and 6.5 minutes for Stage I, whereas reaction time for Stage II was kept constant at 30 mintues. The other operating conditions were maintained the same as mentioned earlier under experimental procedure. It was found that percent coal liquefaction for all Stage I reaction time was about 10 percent higher when the disposable catalyst was used. Similarly, viscosity of product oil, from both Stage I and II, was lower for all Stage I reaction time when the disposable catalyst was used. Product oil from Stage II showed about 35 percent reduction in viscosity with the use of our disposable catalyst in Stage I.

In another set of experiments S.N. 13 through 16, effect of reaction temperature on product oil viscosity from Stage II was studied. Experiments were conducted at reaction time and temperature of 30 minutes and 400°C in Stage II, respectively, with and without the use of the disposable catalyst in Stage I. The first stage liquefaction was conducted at reaction time and temperature of 6.5 minutes and 425°C, respectively. The viscosity of product oil from Stage II was found to be lower by only about 20 percent as compared to 35 percent in earlier experiments S.N. 9 through 12. This is considered due to lower reaction temperature in Stage II.

Solvent analysis (15) was performed on product oil from Stage II for experiments S.N. 14 and 16. It was found that asphaltene content (cyclohexane insolubles) of product oil with no catalyst used in Stage I was 12.3 against 8.3 percent when liquefaction was conducted in Stage I in presence of the disposable catalyst. Preasphaltene (THF insolubles) content was found to be 0.3 percent in both the cases.

Table III

Liquefaction of Coal Using Two Stage Process

Serial Number	Name of Catalyst/Ore	Stage Number	%Catalyst (Based on maf coal/oil)	Reaction Time (mins.)	Reaction Temperature (C)	%Conversion	%Liquefaction	Viscosity, cp @60 C	Difference (% conv.-% Liq.)
1	--	I	--	30	425	85	70	28.5	15
2	Co-Mo Harshaw 0402T	II	1.0*	30	425	--	--	9.8	--
3	Limonite Moly. Oxide Conc. Bauxite	I	1.19 0.572 3.58	30	425	88	82	21.0	6
4	Co-Mo Harshaw 0402T	II	1.0*	30	425	--	--	6.1	--
5	--	I	--	10	425	83	69	42.4	14
6	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30	425	--	--	18.0	--
7	Limonite Moly. Oxide Conc. Bauxite	I	1.19 0.572 3.58	10	425	85	81	31.2	4
8	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30	425	--	--	11.0	--

Table III (cont.)

Serial Number	Name of Catalyst/Ore	Stage Number	%Catalyst (Based on maf coal/oil)	Reaction Time (mins.)	Reaction Temperature (C)	%Conversion	%Liquefaction	Viscosity, cp @60 C	Difference (% conv.-% Liq.)
9	--	I	--	6.5	425	83	69	68.0	14
10	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30.0	425	--	--	22.0	--
11	Limonite Moly. Oxide Conc. Bauxite	I	1.19 0.572 3.58	6.5	425	85	80	38.4	5
12	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30	425	--	--	14.25	--
13	--	I	--	6.5	425	84	70	66.0	14
14	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30.0	400	--	--	29.0	--
15	Limonite Moly. Oxide Conc. Bauxite	I	1.19 0.572 3.58	6.5	425	87	81	36.0	6
16	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30	400	--	--	23.0	--

* Percentage Catalyst Based on Product Oil from Stage I.

Conclusions

The disposable catalyst containing acid treated bauxite, limonite, and molybdenum ore concentrate when used in the first stage of the Two-Stage Liquefaction process improved the yield and quality of product oil. Coal liquefaction yield in Stage I increased by about 10 percent with the use of this catalyst. Similarly, the viscosity of product oil from Stage II showed a decrease of 20-35 percent when the disposable ore catalyst was used in Stage I.

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